

# INFRARED SPECTRA OF STRONGLY HYDROGEN-BONDED SYSTEMS

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In the early spectroscopic work on hydrogen bonding the attention of the investigators was mainly directed to the shifts of the stretching bands. Interest was later extended to the intensity increase and broadening. With stronger hydrogen bonds and better resolution coming into the field the problem of the irregular band shapes and extra peaks arose. Whereas the band shifts and intensity changes are explained by current theories of hydrogen bonding there are still controversies about the breadth and the exact origin of the structure of bands due to the stretching vibration of

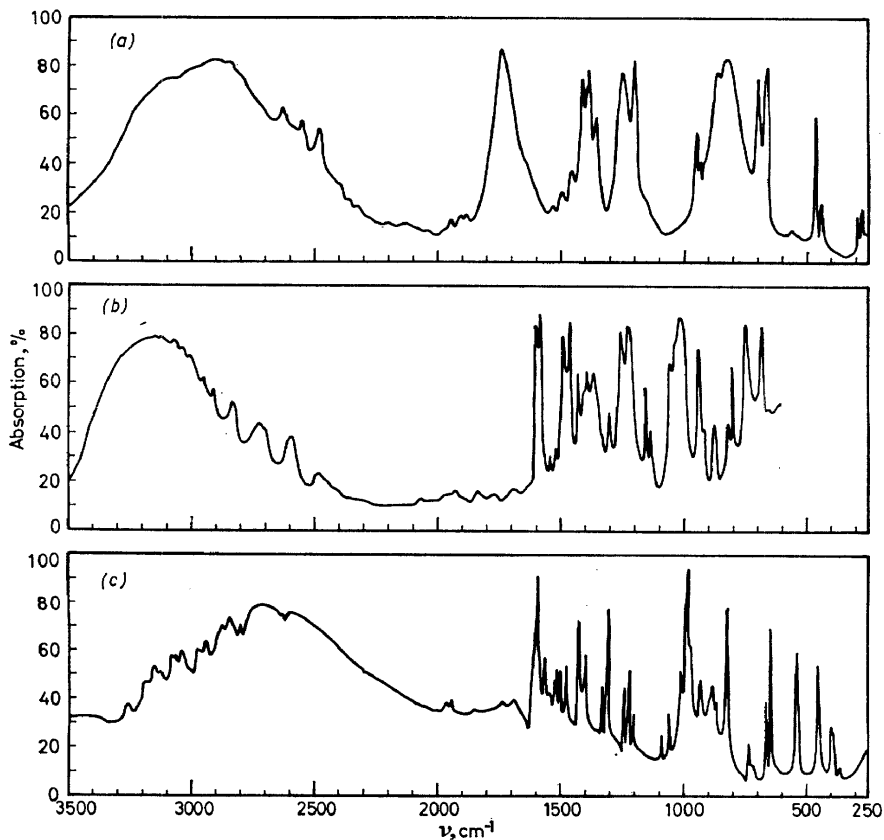


Figure 1. Infrared spectra of (a) trichloroacetic acid (solid); (b) 1 : 1 mixture of phenol and dimethyl sulphoxide (liquid); (c) 4-pyridine aldoxime (solid)

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hydrogen-bonded groups. In connection with the latter problem two groups of examples may reasonably be distinguished. One consists of weaker hydrogen bonds such as exist, *e.g.* in carboxylic acid dimers<sup>1</sup>, amine salts<sup>2,3</sup>, adducts of phenols with bases, and of ethers with strong acids (Figure 1)<sup>4-6</sup>. The other group comprises very strong hydrogen bonds such as those in acid phosphates<sup>7-8</sup>, organophosphoric acids<sup>10,11</sup> *etc.*

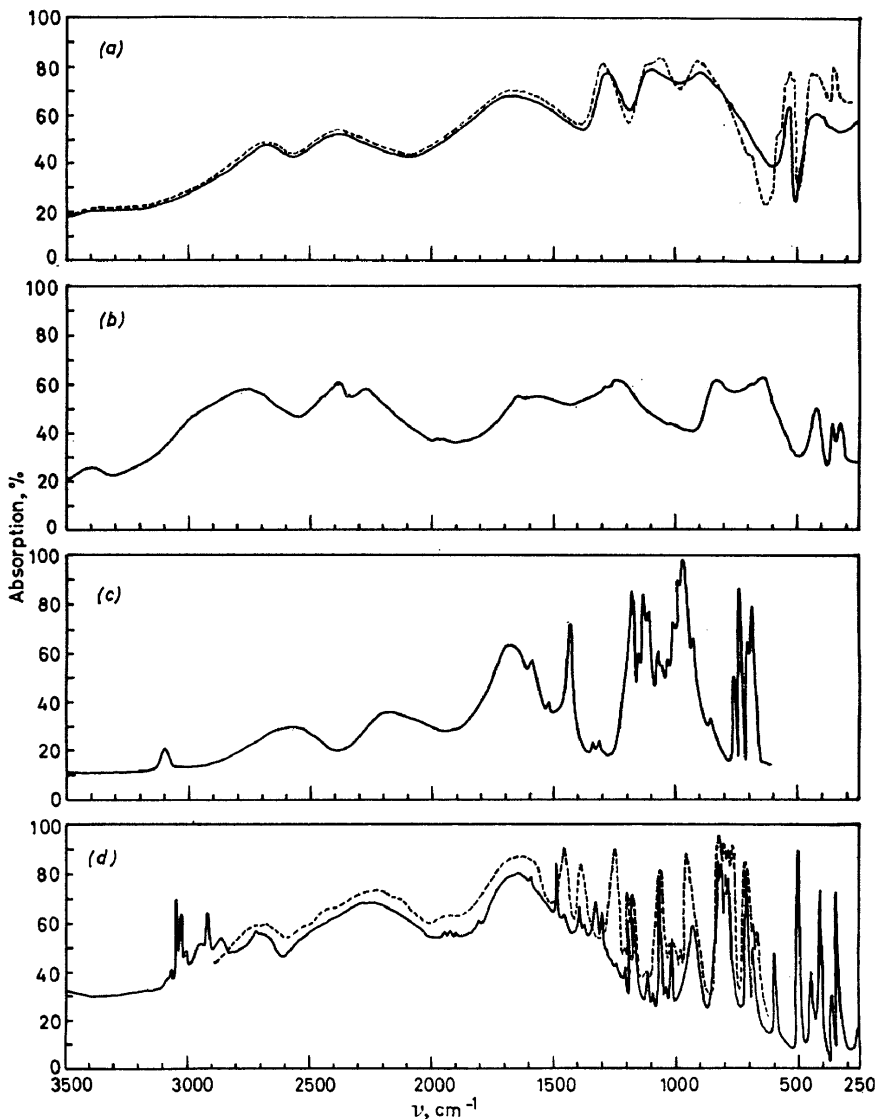


Figure 2. Infrared spectra of (a)  $\text{KH}_2\text{PO}_4$  (— room temperature, ----  $70^\circ\text{K}$ ); (b)  $\text{NaH}_3(\text{SeO}_3)_2$ ; (c) diphenylphosphinic acid; (d) *p*-tolueneseleninic acid (— room temperature, ----  $130^\circ\text{K}$ ); (e) dimethylarsinic acid; (f) potassium hydrogen di(*p*-cyanophenoxide) (g) potassium hydrogen di(*p*-nitrobenzoate); (h) adduct of 3,4 dichloropyridine with dichloroacetic acid. (a)–(g) solids, (h) liquid

Concerning the origin of the extra peaks in the first group, the explanations are not essentially different. Whether extra peaks are attributed to combination frequencies involving internal modes<sup>1,2</sup> or to the Stepanov mechanism<sup>5,12</sup>, the essential condition is anharmonicity<sup>13</sup>. The latter is certainly not without importance for the second type of hydrogen bonds, but here another phenomenon may be invoked which is unlikely to play an important role in the first group. This is the proton tunnelling in a double minimum potential of the hydrogen bond with consequent splitting of vibrational levels. The idea of the double minimum potential may spring from purely intuitive reasoning as well as from theoretical<sup>14</sup> or semi-

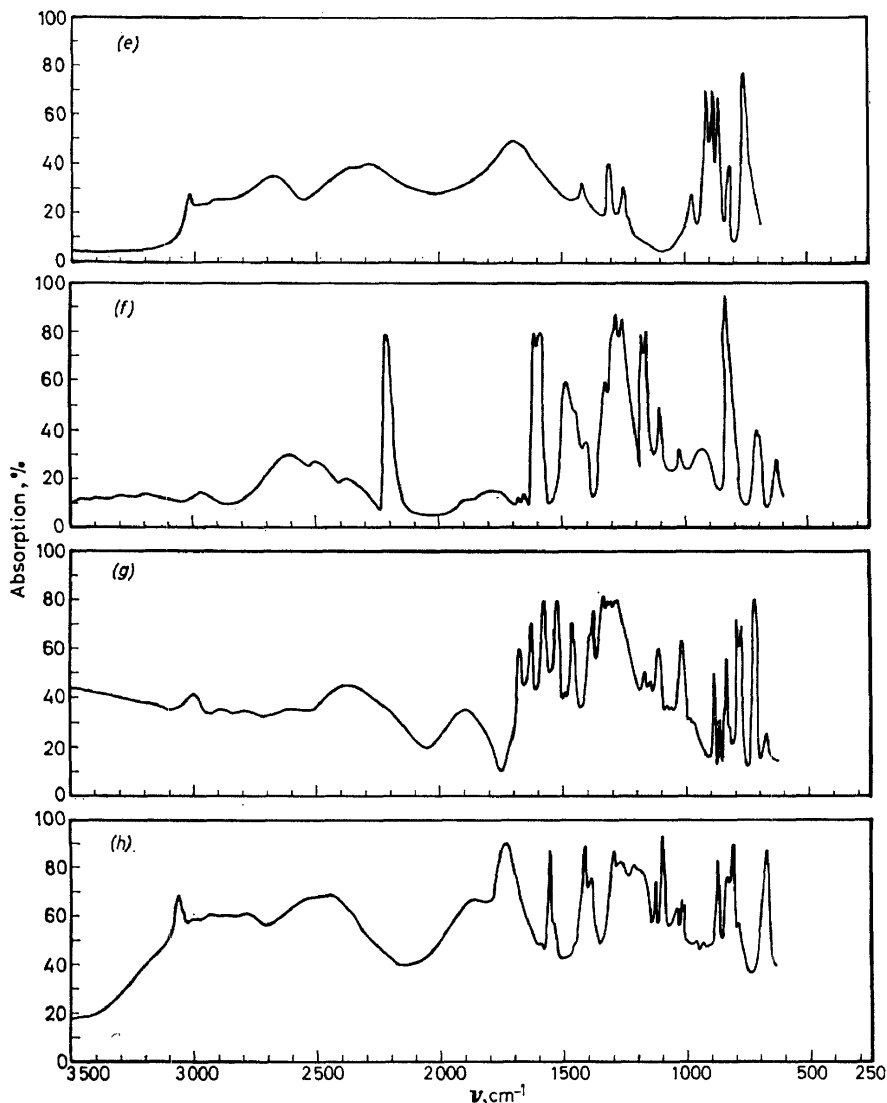


Figure 2—continued

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theoretical deductions<sup>15,16</sup>. From one of the latter<sup>16</sup> it ought to be present for hydrogen bonds above 2.52 Å but for shorter hydrogen bonds the two minima should converge into a single one. The theories and calculations of energy levels are usually developed for simple models—three particles vibrating in one dimension—whereas the real hydrogen-bonded systems have many more degrees of freedom and various types of interactions so that the comparison of real and theoretical spectra is not straightforward. In

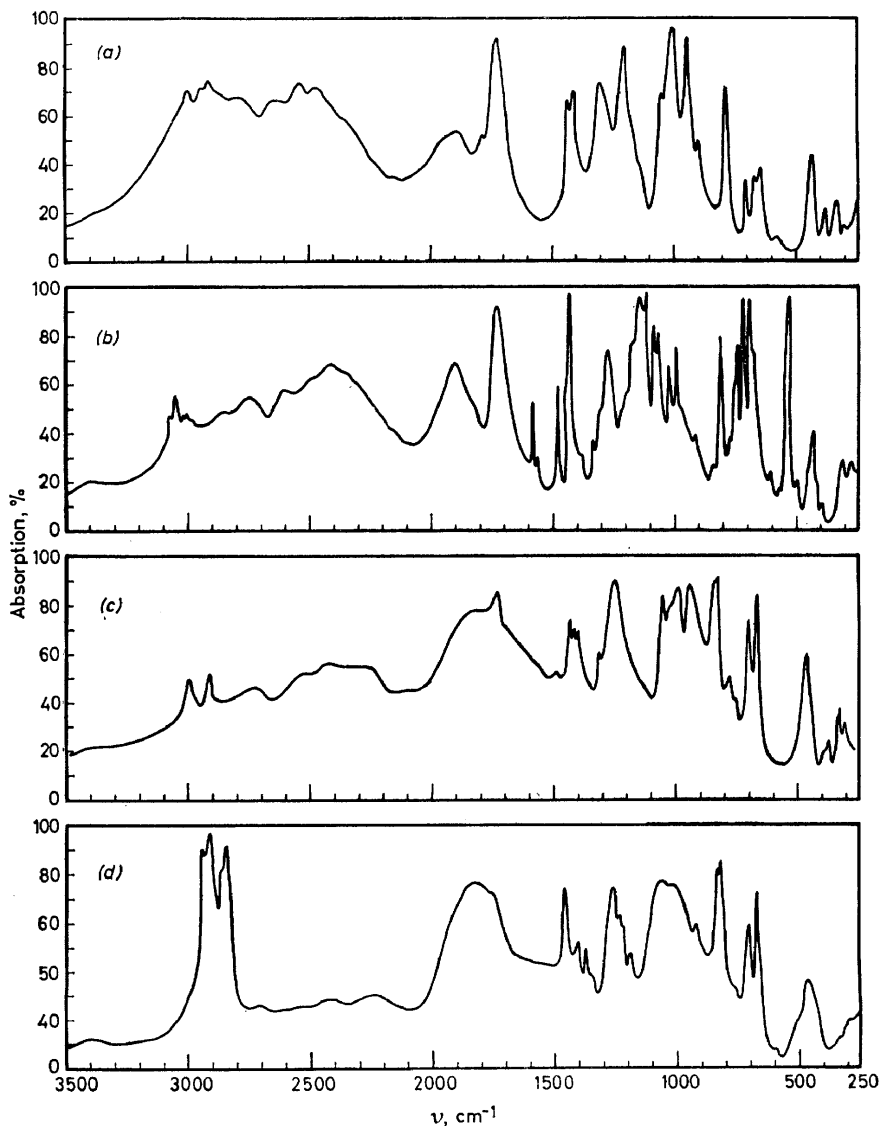


Figure 3. Infrared spectra of (a) monochloroacetic acid and dimethyl sulphoxide; (b) trichloroacetic acid and triphenylphosphine oxide; (c) trichloroacetic acid and dimethyl sulphoxide; (d) trichloroacetic acid and trioctylphosphine oxide (pure liquids)

fact, the spectra of both types and particularly those of the second type have often been considered in connection with tunnelling on the basis of qualitative arguments. However, other explanations are also possible for the appearance of several bands in the stretching region and, in view of the difficulty in finding quantitative agreements between theory and experimental data, it may be interesting to review the latter supplemented by new results† and to discuss them. Of no less interest are the spectra of hydrogen-bonded systems which approach the symmetrical type of bond and the related problem of the reality of the symmetry of these bonds. Thus we shall consider two groups of spectra, both obtained with hydrogen-bonded systems of the OH . . . O type which are extremely strong by all criteria. The shifts of the O—H stretching bands are very large—from 800 to 2000  $\text{cm}^{-1}$  or even more—and the enthalpies are in the range of 10–20 kcal/mole<sup>17</sup>. For some crystallized compounds the O . . . O distances are known and they are within the limits 2.39 to 2.60 Å<sup>18–26</sup>.

The spectra in group (i) exhibit a definite pattern of bands in the region 2900–1600  $\text{cm}^{-1}$  consisting of three main regions of absorption. In some cases they have rather smooth contours, and in others they are split into several sub-maxima. Spectra in group (ii) have no significant bands in this region but show a remarkable broad absorption in the region between 1500 and 600  $\text{cm}^{-1}$ . Group (i) includes a number of compounds which are chemically very different (Figures 2 and 3). The main representatives are dihydrogen phosphates and arsenates such as  $\text{KH}_2\text{PO}_4$  and  $\text{KH}_2\text{AsO}_4$ <sup>7–9</sup>, organophosphoric, phosphinic<sup>11</sup>, seleninic<sup>10</sup>, and arsenic acids, adducts of carboxylic acids and of phenols<sup>27–30</sup> with their conjugate bases or with other appropriate bases, e.g. sulphoxides, and phosphine oxides. Substances yielding spectra of type (ii) are also chemically diverse. Examples have been found amongst complex anions of the type  $(\text{RCOO.H.OOCR})^-$  and  $(\text{RO.H.OR})^-$ <sup>28,29</sup>, complex cations of amine oxides and amides<sup>27,31</sup>, neutral molecules like *p*-dichlorodiphenyl hydrogen phosphate<sup>32</sup>, adducts of carboxylic acids, and phenols<sup>27,29</sup>, with appropriate bases (selenoxides, arsine oxides, amine oxides). Spectra which may be considered intermediate between types (i) and (ii) have also been found and they are useful for the interpretation of the latter.

### SPECTRA OF TYPE (i)

The bands forming a characteristic trio are near 2800, 2500 and 1900  $\text{cm}^{-1}$  if carboxyl groups act as proton donors, but they are somewhat lower (about 2700, 2200 and 1600  $\text{cm}^{-1}$ ) for hydrogen phosphate, arsenate, selenate and similar groups. The behaviour of those bands under various experimental conditions (change of phase, temperature, deuteration, etc.) is quite similar, thus proving that they have an analogous origin. The adducts of the carboxylic acids with various bases are probably the best case for investigation because they permit, besides the previously mentioned changes of experimental conditions, variations of the hydrogen bond strength by proper choice of proton donors and acceptors. It will suffice to select amongst the numerous examples studied<sup>17</sup> only the adducts involving mono-, di-, and trichloroacetic acids (MCA, DCA, TCA) and the bases dimethyl sulphoxide

† Full experimental data and other details will be published elsewhere.

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(DMSO), triphenylphosphine oxide (TPPO), and trioctylphosphine oxide (TOPO). To obtain adducts showing spectra of type (ii) and of intermediates between (i) and (ii) stronger bases such as pyridine-*N*-oxide (PNO), diphenyl selenoxide (DSO), and triphenylarsine oxide are necessary. Without discussing unduly the meaning of acidity and basicity, and their relationship to hydrogen bonding, the strength of the hydrogen bond in adducts would be expected to increase if acids are taken in the order  $MCA < DCA < TCA$  (increasing proton donating ability) and bases in the order  $DMSO < TPPO < TOPO < PNO$ . Their increasing proton-accepting power is shown by larger shifts of the  $\nu_{OH}$  band of methanol<sup>33</sup>. This prediction is borne out by the determinations of association constants and enthalpies<sup>17</sup>. The frequencies of the trio are shown in *Table 1*. With

*Table 1.* Approximate frequencies of the three main bands in the region 1500–3000  $\text{cm}^{-1}$  of some spectra of type (i).

<i>Pure compounds</i>	<i>Frequencies (<math>\text{cm}^{-1}</math>)</i>	<i>Adducts</i>	<i>Frequencies (<math>\text{cm}^{-1}</math>)</i>
$\text{KH}_2\text{PO}_4$	2750	Monochloroacetic acid + dimethylsulphoxide	2900
	2400		2545
	1580		1900
$\text{Ag}_2\text{H}_3\text{IO}_6$	2560	Monochloroacetic acid + triphenylphosphine oxide	2800
	2150		2540
	1540		1900
$\text{NaH}_3(\text{SeO}_3)_2$	2750	Dichloroacetic acid + dimethylsulphoxide	2880
	2350		2440
	1600		1875
Dibutylphosphoric acid (liquid)	2650	Dichloroacetic acid + triphenylphosphine oxide	2750
	2280		2430
	1680		1900
Dibutylphosphinic acid (solid)	2600	Trichloroacetic acid + dimethylsulphoxide	2750
	2240		2430
	1630		1880
Tolueneseleninic acid (solid)	2720	Trichloroacetic acid + triphenylphosphine oxide	2720
	2270		2400
	1660		1900
Dimethylarsinic acid (solid)	2700		
	2350		
	1740		

increasing bond strengths, the bands near 2800  $\text{cm}^{-1}$  (band *A*) and 2500  $\text{cm}^{-1}$  (band *B*) assume lower frequencies whereas the third band (*C*) remains firm. Even more spectacular than the shifts are the simultaneously occurring intensity changes (*Figure 3*). Whereas bands *A* and *B* decrease in intensity, band *C* increases. The intensity determinations are rather crude because of the breadth and overlapping of bands but the trends in the ratio of the band intensities *A* + *B* and *C* are more reliable. For example this ratio for the adducts of MCA, DCA, and TCA with DMSO in carbon tetrachloride solution is 9.1, 4.0 and 2.6, respectively. With stronger bases the ratio is even more in favour of band *C* which takes over most of the intensity in the adduct of TCA with TOPO. The total absorption of all three bands amounts to more than it is for the  $\nu_{OH}$  band of the acid dimers. The increase is from 30 to 100 per cent depending upon the strength of the adduct.

In most examples studied which include also organophosphoric and phosphinic acids<sup>11</sup> there are no essential differences in the trio of solids and

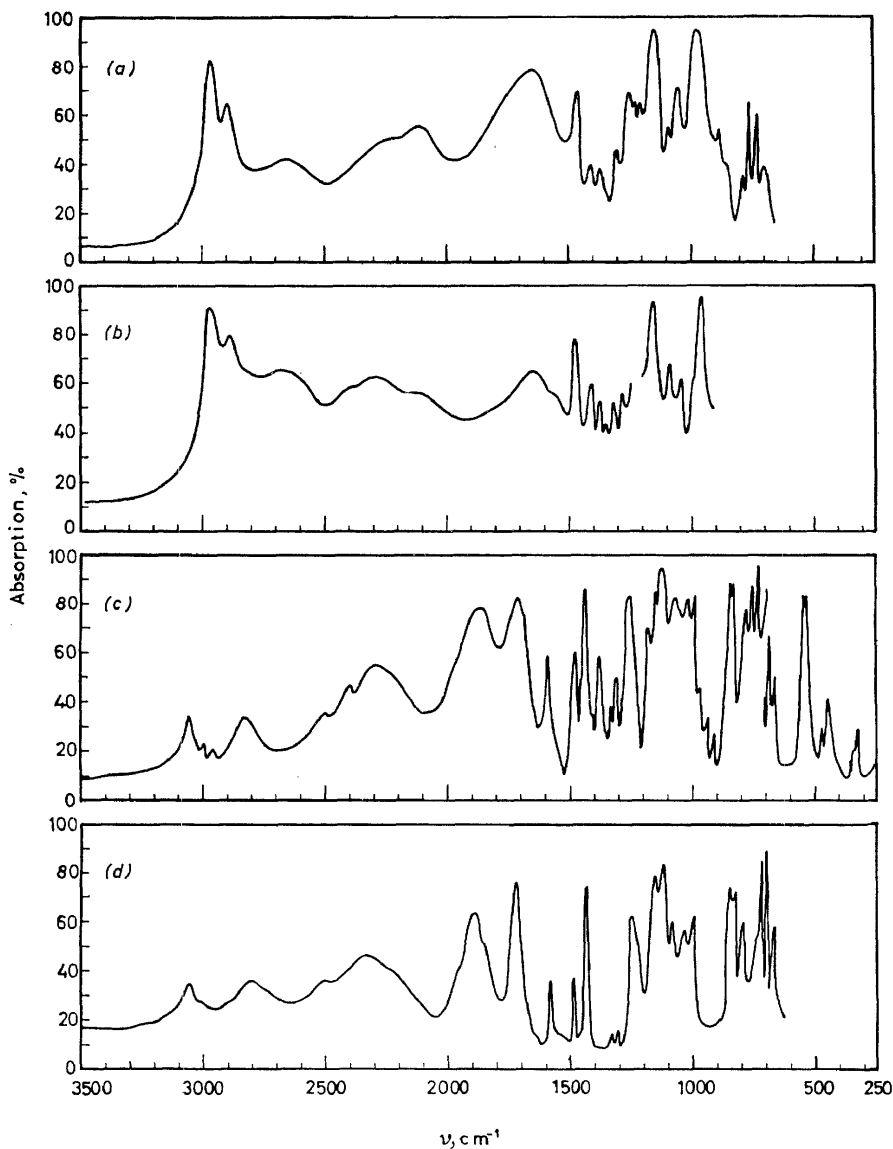


Figure 4. Infrared spectra of (a) dibutylphosphinic acid (solid); (b) dibutylphosphinic acid (solution in chloroform); (c) the adduct of triphenylphosphine oxide with trichloroacetic acid (solid); (d) the adduct of triphenylphosphine oxide with trichloroacetic acid (solution in chloroform)

corresponding liquids or solutions (Figure 4; See also Figure 3c and Figure 5a). There is, however, a tendency of band C to become weaker on passing from a pure compound or adduct to the corresponding solution but this is not continued on further dilution down to very low concentrations. These observations are, of course, limited to substances which can be melted and

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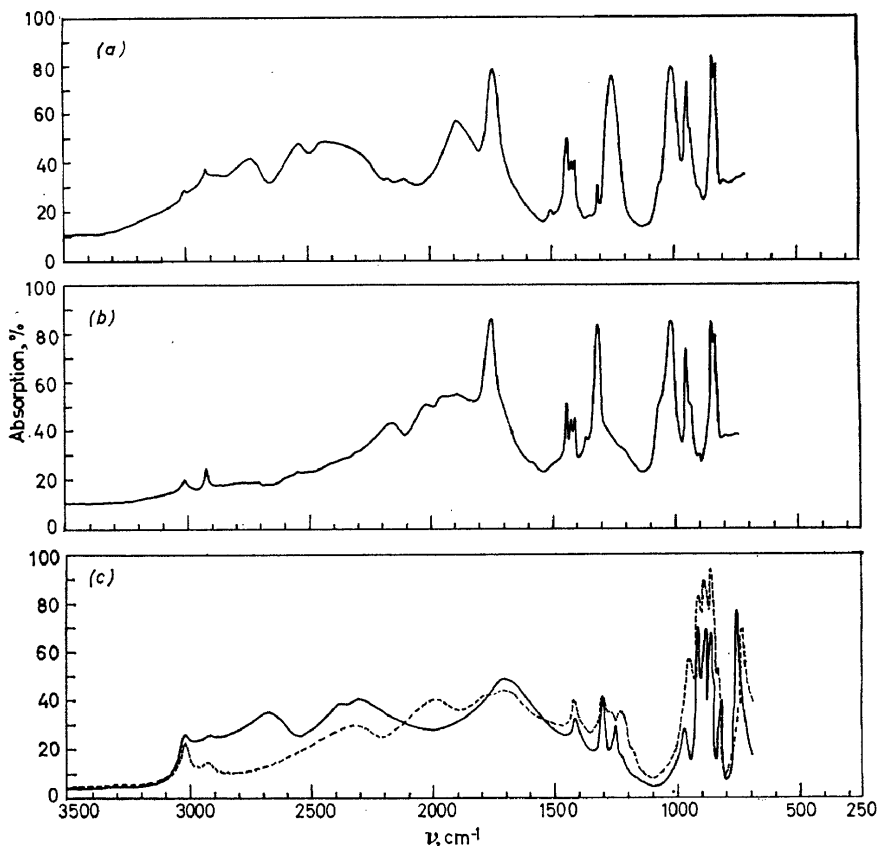


Figure 5. Infrared spectra of (a) the adduct of trichloroacetic acid with dimethyl sulphoxide (0.3 M in carbon tetrachloride); (b) the adduct of trichloroacetic acid with dimethyl sulphoxide (deuterated, 0.3M in carbon tetrachloride); (c) dimethylarsinic acid (— normal, ---- deuterated)

dissolved in appropriate solvents. Cooling down to liquid nitrogen temperature and even to liquid helium temperature ( $\text{KH}_2\text{PO}_4$ , Figure 2d) does not essentially influence either the frequency or the intensities of the trio. There is certainly no decrease in relative intensity, and that of band C may even be slightly increased (*e.g.* tulueneseleninic acid, Figure 2d). The changes in the trio imparted by deuteration are very important for the discussion of its origin, but not easy to sort out. There is no doubt that bands A and B disappear with deuteration (Figure 5) and that a new band appears near  $2000\text{ cm}^{-1}$ . With carboxylic acid adducts the frequency of this band is remarkably constant ( $2155 \pm 25\text{ cm}^{-1}$ ). The frequency tends to be lower for stronger adducts. With the phosphates, seleninic acids *etc.*<sup>10,11</sup> this band appears at about  $1970\text{ cm}^{-1}$ . There is a good correlation between the frequency of this band and of band A, the ratio being close to 1:1.3 or rather more. If band B had shifted on deuteration by a similar factor it would heavily overlap the region of band C. This in fact seems to be occurring. The peak absorption in most cases is sufficiently different from



that of the former band *C* and there may also be an intensity increase to show that band *B* has moved. The frequency ratio tends to be slightly less than 1.3 with carboxylic adducts, but more than this for the others. The fate of band *C* is much more problematical. With carboxylic adducts and organophosphoric acids no corresponding band can be detected at lower frequencies. In the case of seleninic<sup>10</sup> and arsenic acids (*Figure 5c*) a much weaker band appears near 1248 and 1260  $\text{cm}^{-1}$ , respectively. Such a weak band would easily escape observation in the former two types of compounds.  $\text{KD}_2\text{PO}_4$  also exhibits a new weak band<sup>7</sup> near 1200  $\text{cm}^{-1}$ . In view of the great difference in intensity the correlation of this band and band *C* is open to doubt. Even so, there is good evidence that band *C* disappears or at least becomes very much weaker after deuteration. The ratio of the intensities of bands *A* + *B* + *C* in normal diphenylphosphoric acid, dibutylphosphinic acid<sup>11</sup>, DCA-DMSO, and TCA-DMSO adducts to that of the corresponding new, complex absorption in the deuterated analogues is very near to 0.5. The experimental facts clearly demonstrate the intimate connection of the trio with proton movements but do not show which particular ones are involved. It has been suggested<sup>34</sup> that band *C* should be connected with an O-H deformation vibration. This is unlikely with respect to its deuteration behaviour and particularly in view of the fact that such vibrations are located elsewhere<sup>10,11</sup>. The deformation vibrations will be considered later and the trio will now be discussed from the point of view of stretching. Several common reasons for the appearance of multiple stretching bands, such as crystal interactions or the simultaneous occurrence of different types of hydrogen bonds, are easily eliminated remembering the afore-mentioned behaviour of the bands on passing from the solid state to solution. It has also been possible to prepare mixed crystals of  $\text{KH}_2\text{PO}_4$  with some other isomorphous phosphates and arsenates and crystals with different H/D isotopic ratio<sup>17</sup>. No significant influence on the bands of the trio was observed. The mixtures of carboxylic acids with bases might contain adducts of different composition and also proton transfer products. Neither of them showed up in the determination of equilibrium constants<sup>17</sup> or of dielectric constants<sup>35</sup>, nor do any characteristic bands of proton transfer products appear in the other regions of infrared spectra. Amongst the less common reasons for the appearance of multiple OH bands the splitting of vibrational levels due to the proton tunnelling has attracted considerable attention<sup>10,36-39</sup>. Particularly suitable for this kind of treatment appear to be the hydrogen-bonded ferroelectrics of the  $\text{KH}_2\text{PO}_4$  type<sup>7,8</sup> in which the polarization properties are intimately connected with proton tunnelling<sup>40,41</sup>. This kind of motion has been proved directly<sup>42</sup>. For the hydrogen bonds in acid-base adducts one would expect intuitively a double minimum potential. In both cases the potential should be asymmetrical. However, the causes of the asymmetry are different in each system. If the hydrogen bond is connecting a proton donor and acceptor which are related between them as an acid and its conjugated base (*e.g.*  $\text{KH}_2\text{PO}_4$  and many other acid salts) the asymmetry is introduced by proton-lattice and proton-proton interactions. In the case of chemically different proton donors and acceptors (acid-base adducts other than between an acid and its conjugated base) the asymmetry is related mainly to the difference between the occupied and the vacant

proton levels. This difference in the cause of asymmetry will be important in the following discussion, but for the moment it is necessary to consider what can in principle be inferred from asymmetric double minimum potentials. The selection rules for transitions amongst the lowest levels in such a potential permit four of the infrared active type. The separation between the corresponding bands, their intensity and deuteration shifts depend upon the exact shape of the potential. Due to low intensity or small separation only three or fewer bands may be found under certain circumstances. It is a very difficult task to show for, say, three bands such as the presently discussed trio, that they are related to such transitions. This is even more so if the bands are observed in an isolated example or with closely related systems only. For positive proof it is necessary to obtain close agreement between the results of calculations on a suitable model potential and the observed spectrum. The agreement should actually extend to several overtones because of the possibility of fortuitous coincidences with bands having different origins. However, the chances of such agreement are very slim for it is necessary to have either a very good model to start from or to carry out an immense number of calculations in view of the large number of physically possible double minimum situations and lack of initial data. Moreover there is a difficulty concerning the overtones. With substances mentioned in this paper no bands above  $3000\text{ cm}^{-1}$  were detected<sup>17</sup> which could be ascribed to OH overtones. If they exist at all they must be extremely broad and thus be hidden by other bands. However, qualitative comparisons, particularly those concerning temperature and deuteration effects, can be made of existing spectra; the rather extensive calculations on a simple model executed by Somorjai<sup>43</sup> and supplemented by Pshenichnov and Sokolov<sup>44</sup>.  $\text{KH}_2\text{PO}_4$  is suited for this because the asymmetry is known<sup>42</sup> to be  $625\text{ cm}^{-1}$  and the splitting of the lowest levels is estimated to be less than  $100\text{ cm}^{-1}$ . This clearly cannot yield the observed trio. It may be assumed that the actual form of the potential is different from the model and therefore that the energy levels are different. This would invalidate the comparison. It is still however possible to consider temperature effects and structural factors. For an asymmetric potential, one of the bands ought to contain the  $1 \rightarrow 2$  transition. This should have the lowest frequency in the group of "fundamental" transitions ( $0 \rightarrow 2$ ,  $0 \rightarrow 3$ ,  $1 \rightarrow 2$ , and  $1 \rightarrow 3$ ). Because it is a "hot" band its intensity should decrease on cooling. Such a decrease has not been observed even at  $70^\circ\text{K}$ . Especially in the case of the ferroelectrics there should be a very pronounced change in the trio when the temperature is lowered below the Curie point. The trio is connected with transitions in the double minimum potential because of the changes in the proton lattice interactions and the consecutive change in the effective asymmetry of the potential near the phase transition. The confrontation of the spectra of  $\text{KH}_2\text{PO}_4$  and the isomorphous salts with those of organophosphoric acids is also very instructive. In the former, the hydrogen bonds form a network in which closed loops of proton jumps are possible whereas, for instance, dibenzylphosphate and the seleninic acids contain hydrogen-bonded chains without such loops<sup>45,46</sup>. Further, in contrast to the organophosphoric acids the inorganic phosphates have an ionic lattice. This means that the proton-lattice and the proton-proton interactions should be considerably different

for each type of system, the latter type of interaction being the strongest for chains<sup>47</sup>. Since the asymmetry depends mainly on these interactions, this should be strongly reflected in the frequencies and intensities of the trio. The transition from solid to solution which is experimentally possible only with the organophosphoric acids should also cause large differences in these interactions because in this transition not only the chains become separated but dimers are formed<sup>48</sup>. This should also greatly influence the interactions. Since the asymmetry in these examples depends upon various types of proton-lattice and proton-proton interactions, the band frequencies and intensities of the trio should be rather different for both types of phosphates and particularly for solids and solutions, respectively.

The arguments about the asymmetry have to be put in slightly different terms for the acid-base adducts. Here the proton-lattice and other interactions play a subordinate role, particularly for liquids. Although there is practically no initial quantitative data for a model of the potential function, we may safely assume that its asymmetry increases in the adducts in the order  $TCA < DCA < MCA$ . From the differences between the proton levels of the donors and acceptors as estimated from acidities<sup>58</sup>, it is expected that the differences between the potential minima would change for over a thousand wavenumbers. The accompanying changes in the distances between the minima and in the size of the potential barrier are probably such that they increase the effects of the asymmetry on the energy levels which should be affected quite substantially. The observed small variations in frequency of the bands constituting the trio are therefore a definite argument against its connection with transitions in a double minimum potential. It can be argued that it is an oversimplification to use potential models with static character, *i.e.* with fixed O . . . O distance. In fact, model calculations show that OH . . . O motions should strongly affect the OH "stretching vibration". Phillips and Bratož<sup>49</sup> have made a quantum mechanical calculation of the energy levels of a simple model using the Reid potential<sup>16</sup> with the result that the O-H stretching develops into a complex absorption pattern. Blinc and Svetina<sup>41</sup> also predict the appearance of several complex bands in the high-frequency region of the spectrum of hydrogen-bonded crystals with strong proton-lattice interactions and proton tunnelling. It is again very difficult to decide whether the observed bands correspond to the theoretical spectrum or not, unless a reasonable numerical agreement is obtained or definite trends in band frequencies and intensities are observed when varying the parameters which define the potential. Such variations are, of course, difficult to achieve in real hydrogen-bonded systems. A qualitative argument against the explanation of the origin of the trio in terms of any intermolecular motions is the fact that it appears with such constancy throughout so many examples of great variety of masses, crystal structures and under different states of aggregation. This fact is difficult to reconcile with any theory based on vibrations sensitive to mass and to intermolecular forces. However, it does not mean that such vibrations do not contribute to the detailed band shapes including minor splittings.

Remaining for discussion of the possible origins of the trio are combinations involving internal vibrations. The relatively small variability of frequencies and the deuteration behaviour of the trio require that the frequencies of the

fundamentals, the combinations or overtones of which should be considered, be both constant and sensitive to deuteration. In the spectra of carboxylic acids and their adducts there are indeed two bands with appropriate frequencies and of surprising constancy; one is near 1280 and the other near 1400  $\text{cm}^{-1}$ . They are assigned to coupled CO stretching and OH deformation modes<sup>50</sup>. The overtone of either of them, but more likely of the second, or their combination frequency are appropriate to mix with the OH stretching fundamental. The latter is expected to be, if unperturbed, near 2700  $\text{cm}^{-1}$  for the weaker adducts. Its interaction with the previously mentioned overtone would yield two bands displaced towards higher and lower frequencies, respectively. The interaction is probably conditioned by strong anharmonicity which, however, makes more exact estimations of frequencies and intensities rather useless. The change to lower frequencies of the unperturbed OH stretching vibration which is likely to be brought about by the increasing strength of hydrogen bonding throughout the series of adducts will influence the extent of mixing and thus the frequency and intensity trends observed with bands *A* and *B*. It is possible that with the weaker adducts band *A* is predominantly O-H stretching in character and in the strongest adducts band *B* takes this over. The lower frequency of bands *A* and *B* in the series of phosphoric, seleninic and arsenic acids would be in agreement with this since here the OH deformation band is also found at lower frequencies<sup>10,11</sup>. Unfortunately, the frequency of the latter is not easily determined in phosphoric acids and therefore its trends cannot be well compared with those of bands *A* and *B*. The origin of band *C* is difficult to explain on the same basis although the  $\gamma$ -OH out-of-plane deformation in carboxylic acids<sup>50</sup> yields an overtone near 1900  $\text{cm}^{-1}$  or lower. This is quite distant from the OH stretching frequency, particularly for the adducts with weaker bonding. The other difficulty lies in the fact that there is no connection between the intensity increase and the assumed approach of the frequency of OH stretching which is required if the band *C* is to borrow its intensity by Fermi resonance from the latter.

Actually it is not necessary to have strong (fundamental) deformation vibrations in order to have strong overtones and to have both mechanical and electrical anharmonicity, the latter alone being sufficient<sup>51</sup>. Although the assumption of strong electrical anharmonicity may explain the origin of band *C*, the additional assumption of a different anharmonicity for O-D vibrations is necessary to account for the much lower intensity of this band in the deuterated analogues. There is no other evidence for this and unfortunately there is altogether too little knowledge about the dipole moment function of the hydrogen bond, and particularly of its deformation vibrations, to carry these arguments further. It is only necessary to point out that the deformation vibrations in some strong hydrogen bonds have low intensity. This has also been observed previously<sup>27</sup>, but in the adducts it seems to be pushed to the extreme (as will be described in a later paragraph) and the decrease of the intensity of deformation vibrations contrasts the intensity increase of the trio with increasing bond strength and also the increase of the static dipole moment on adduct formation<sup>35</sup>. The discussion of the possible origins of the trio has shown that no single explanation is completely satisfactory. The last mentioned explanation points, however,

to the necessity of considering three dimensional models with strongly anharmonic surfaces.

### SPECTRA OF TYPE (ii)

The crystal structure of several compounds exhibiting this type of spectrum is known<sup>18-21,25,52</sup>. In all these cases, the centre of the hydrogen bond coincides with either a crystallographic centre of symmetry or with a two-fold axis. The crystal structure conditions for symmetric hydrogen bonds are thus given. So far there is regular coincidence of this type of structure with the unusual infrared spectrum, the main feature of which is the broad and strong absorption in the region 600–1500  $\text{cm}^{-1}$ . The appearance of this absorption was successfully used for predicting the existence of such structures<sup>21,52</sup>. However, the problem still persists as to whether these structures contain symmetrical hydrogen bonds with a single central potential minimum since the crystallographic findings, including those obtained by neutron diffraction<sup>25</sup>, are just as compatible with two potential minima of small separation and statistical symmetry only. The associated questions are what the spectrum of a genuine symmetrical hydrogen bond should be like and, if the spectra of type (ii) do not correspond to this, how else they can be interpreted.

The truly symmetrical hydrogen bond should be represented by a nearly harmonic potential function. This requires that the  $\nu_3$  mode (asymmetric O—H—O stretching) should show a H/D frequency ratio very near 1.4 as is in fact observed with the  $\text{FHF}^-$  ion. The main problem in dealing with spectra of type (ii) is then the search for the band corresponding to this vibration. The examination of a substantial number of spectra of this type did not reveal it. In fact, it is one of the main characteristics of these spectra

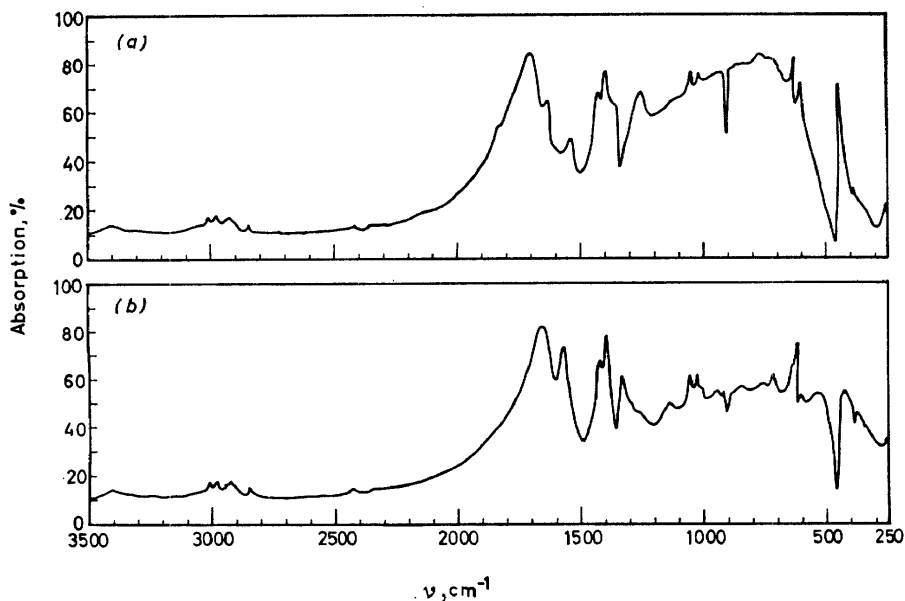
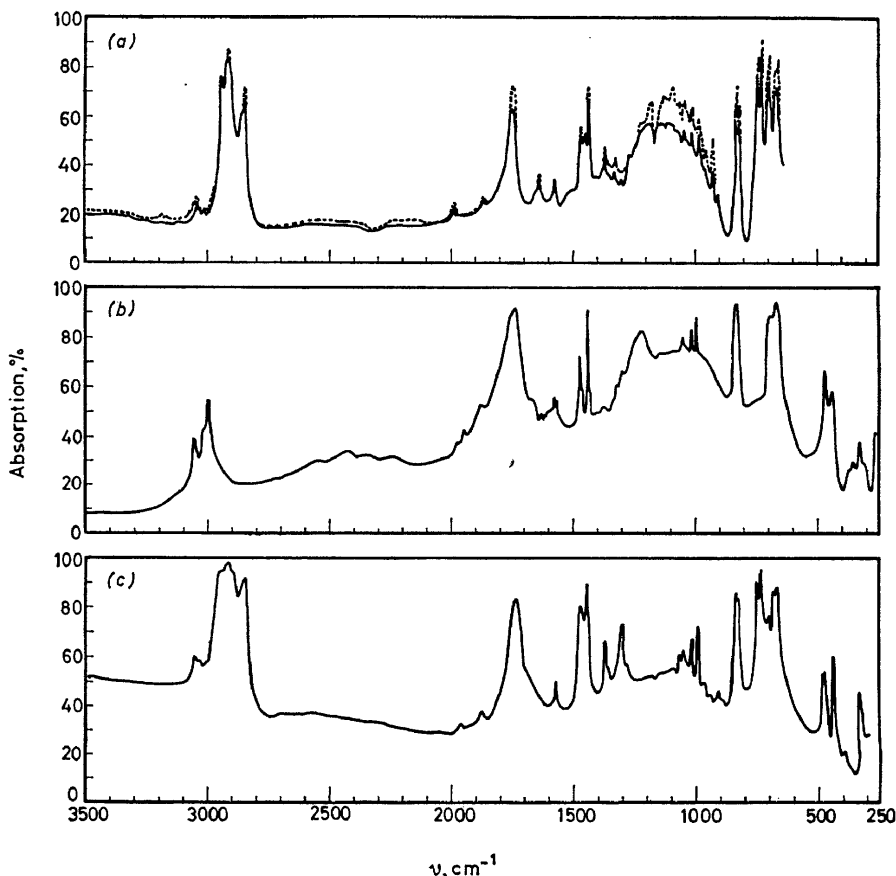


Figure 6. Infrared spectra of (a) sodium hydrogen diacetate; (b) sodium deuterium diacetate

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that there is no band which could be assigned on the basis of the usual criteria, to an OH stretching vibration. There is, however, the broad absorption (which will be designated as band *D*) which is certainly connected with this particular type of hydrogen bonding, though its origin remains as yet unexplained<sup>28</sup>. Band *D* shows definite changes on deuteration. Its intensity decreases by some 40 per cent and it even seems to shift to lower frequencies. Both the intensity change and the shift are difficult to follow because of the very irregular shape of the absorption and interference from other bands. The shift is particularly clearly observed in the case of sodium hydrogen diacetate (*Figure 6*), but it is almost non-existent in the case of the adduct of TCA with diphenylselenoxide. Besides band *D* a flat and broad band is observed near 2400  $\text{cm}^{-1}$  in the latter case (*Figure 7*), and in other adducts, *e.g.* of TCA with PNO and with triphenyl arsinoxide. It disappears after deuteration but its deuterium analogue cannot be detected. This is not surprising in view of the low band intensity and the occupation by other bands of the region to which it should have been displaced. Consider now



*Figure 7.* Infrared spectra of the adduct of trichloroacetic acid with diphenyl selenoxide. (a) solid (— room temperature, ---- 130°K); (b) solution in chloroform; (c) solid, deuterated

what type of potential curve may be expected for the adducts showing spectra of type (ii). Although the occupied and vacant proton levels may be very similar, it is unlikely that they are identical for a substantial number of acids and bases of different structure and, moreover, that the minima in the potential function be separated by a vanishingly small barrier. Thus, the adducts are unlikely to contain symmetrical hydrogen bonds. One would expect the potential curve to have a deeper minimum for the proton on the side of the acid, and another shallow one on the side of the base, because there is no indication of a carboxylate ion in the spectra. If the top of the barrier happens to be near the first excited level, the isotope shift for the transition to this level may be very small as shown by Somorjai<sup>43</sup>. For the overtones which have a much smaller intensity the isotope shift is more pronounced. Such a situation would fit the spectral findings. Band *D* would thus represent the  $0 \rightarrow 1$  transition and the weaker one the  $0 \rightarrow 2$  transition. It may be questioned whether band *D* is a genuine band or just the result of an unusual broadening of bands due to vibrations other than the stretching in the hydrogen bond. Some further adducts illustrate this point (*Figure 8*). The spectra of MCA and DCA bonded, *e.g.* to PNO show that the bands in the region  $1000\text{--}1450\text{ cm}^{-1}$  are in fact considerably broadened. However, they can still be individually assigned to known bands of the carboxyl group and to N—O stretching. On the other hand, the adduct of TCA with *t*-butyl sulphoxide shows a genuine broad band extending from about  $2000$  to  $1300\text{ cm}^{-1}$ . This and the adduct of the same acid with TOPO (*Figure 3d*) may be considered as transitions between spectra of type (i) and (ii) and may illustrate the evolution of the curious absorption from a genuine band, likely to be due to the O—H stretching vibration, and the broadened bands originating in other vibrations of groups closely related to the hydrogen bond. The total intensity of band *D* is of the same order of magnitude as the sum of bands *A*, *B*, and *C* in spectra of type (i). This cannot be taken as strict proof of the above assignment but it makes it consistent with the inference that in this series of adducts the hydrogen bond strength increases with subsequent shifting of the O—H stretching frequency near to  $1000\text{ cm}^{-1}$ . If the interpretation of the spectra of such strongly bonded adducts is carried over to the case of acid salts with symmetrical structures<sup>20</sup> (Speakman's type *A*) one is led to the conclusion that here also the hydrogen bond is not strictly symmetrical. This deduction can be supported by the very different behaviour of band *D* and the  $\nu_3$  band in  $\text{FHF}^-$  on deuteration if the latter is taken as representative of truly symmetrical hydrogen bonds. Also, the spectrum of the acid maleate ion<sup>28, 54</sup> has nothing quite comparable to band *D* and this ion is most likely to contain a truly symmetrical hydrogen bond. However, this deduction appears to be in disagreement with previously reached conclusions<sup>28</sup> about the hydrogen bond in type *A* salts. The previous assignment of a frequency near to the O—H stretching ( $1660\text{ cm}^{-1}$ ) is not crucial as it might just as well be considered as its overtone as proposed above for the band near  $2400\text{ cm}^{-1}$  in spectra of the adducts; but the absence of carboxylate ion bands is a firm argument against any potential which requires the proton to be nearer to one carboxylic group. A reconciliation between these apparently conflicting requirements may perhaps be found in some odd-shaped potential surface

## INFRARED SPECTRA OF STRONGLY HYDROGEN-BONDED SYSTEMS

which would account also for the proton-lattice interactions. The infrared spectra alone cannot give enough information for the construction of such a surface, but they are nevertheless a very useful tool for the detection of unusually strong hydrogen bonds and for their classification into various categories.

So far only the bands associated with what is colloquially termed the O—H stretching have been considered. It is interesting also to examine briefly the

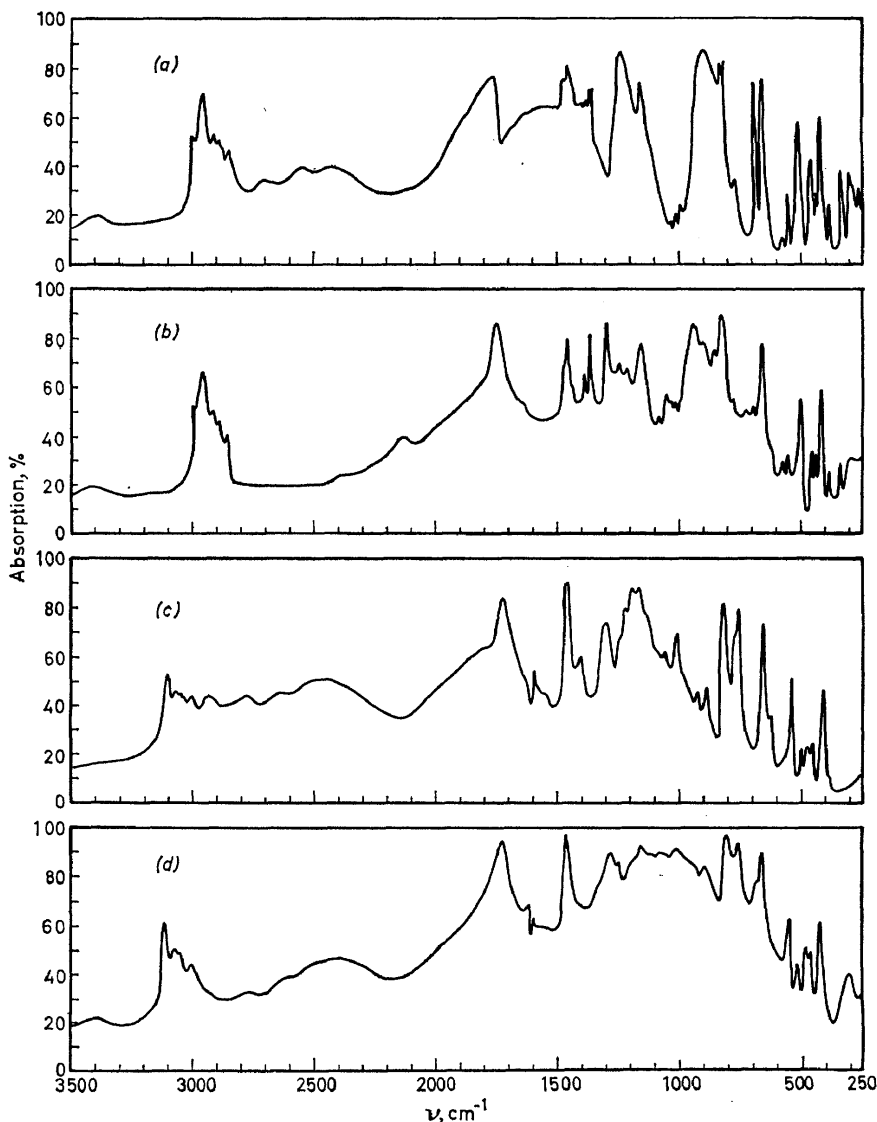


Figure 8. Infrared spectra of adducts of (a) *t*-butyl sulphoxide with trichloroacetic acid (solid, normal); (b) *t*-butyl sulphoxide with trichloroacetic acid (solid, deuterated); (c) pyridine-*N*-oxide with monochloroacetic acid (liquid); (d) pyridine-*N*-oxide with dichloroacetic acid (liquid)



bands due to deformation vibrations. These should progress towards higher frequencies with increasing strength of the hydrogen bonds<sup>55</sup>. This appears to be true only to a certain limit<sup>56</sup> and, in contrast to the behaviour of the stretching vibration, further increase in the hydrogen bond strength causes no more shifting. A really systematic investigation of the behaviour of the "in-plane" deformation vibration is difficult to carry out because of its coupling with other vibrations in most compounds or on account of difficulties connected with its detection. One deformation band can be identified in the spectra of  $\text{KH}_2\text{PO}_4$ <sup>7,9</sup> and related salts<sup>7</sup> and also in those of seleninic<sup>10</sup> and arsenic acids. In all these cases it is located between 1240 and 1300  $\text{cm}^{-1}$ . Organophosphoric acids appear to have this band near 1230  $\text{cm}^{-1}$ . The adducts of carboxylic acids with bases might be expected to yield suitable material for this kind of investigation because of the possibility of gradually changing the strength of hydrogen bonding. Unfortunately, this expectation is not borne out because of the already mentioned loss of intensity of the deformation bands in the stronger adducts. There is, however, an indirect way of showing that at least one of the deformation frequencies is not affected by the increasing strength of bonding. It is well-known from previous investigations<sup>50</sup> of the spectra of carboxylic acids that the in-plane deformation vibration is strongly coupled to the C—O stretching. The two bands corresponding to these coupled modes are near 1300 and 1400  $\text{cm}^{-1}$ . Deuteration uncouples the two vibrations and the predominantly C—O vibration then appears near 1350  $\text{cm}^{-1}$ . The strong band near 1300  $\text{cm}^{-1}$  can still be found in the spectra of the adducts at very nearly the same frequency as with pure acids and shows also the same change on deuteration. This indicates that the vibration to which the C—O stretching was coupled must have preserved its frequency in the adduct also even if the intensity was so reduced that the band virtually disappeared from the spectrum. This confirms other indications that at least one of the deformation vibrations does not shift further upon increasing the strength of hydrogen bonding. The other deformation (out-of-plane) is also too weak to be observed in the adducts. However, this is not so with a number of acid salts and from such spectra it can be concluded that this vibration does progress towards higher frequencies with increasing hydrogen bonding<sup>57</sup>. This brings to an end the results of this series of investigations into the characteristics of the spectra of strongly hydrogen-bonded systems. Several important points have not been considered such as, for instance, the low-frequency vibrations in the hydrogen bond. Although experimental facts on such points are accumulating at an increased rate with the availability of far-infrared spectrometers, there are not as yet enough screened and systematic data for correlative discussions. The ubiquitous problem of the broadness of bands in hydrogen-bonded systems has also been omitted because no illuminating new experiments or ideas have been produced in the last few years.

*The financial assistance of the Federal Research Fund and the Fund Boris Kidrič is gratefully acknowledged. The author thanks also Drs. N. Kobilarov, A. Novak, S. Detoni and Mr. A. Ažman for their collaboration, Mr. F. Cvek for his invaluable help in experimental work, Dr. L. Sobczyk for the communication of his results with dielectric measurements, and Dr. Szafran for his gift of diphenyl selenoxide.*

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